

Solid State Communications, Vol. 24, pp. 295-297 1977. Pergamon Press. Printed in Great Britain

OPTICAL PROPERTIES OF F CENTERS IN KCN CRYSTAL

J.-P. von der Weid*, M. Nsabimana and M. Aegerter

Institut de Physique, Université de Neuchâtel, Rue A.-L. Breguet 1,
CH - 2000 Neuchâtel, Switzerland

(Received 10th July by G.F. Bassani)

Absorption, excitation and emission spectra of F centers in KCN were measured between 4.5 K and 175 K. Due to the cubic to orthorhombic structural phase transition at 168 K, the F band splits into three components. Their properties in the antiferroelectric phase ($T < 83$ K) are explained by an internal Stark effect due to the local electric field. The single emission band has a decay time of 21.5 nsec at 4.5 K.

The properties of alkali-cyanides crystals such as crystalline structure¹, specific heat², dielectric constants³ and Raman scattering⁴ have been recently studied in a large range of temperature. From temperatures just below the melting point down to 168 K, pure KCN crystals present the cubic NaCl type structure, due to the rapid reorientation of the CN^- ion group. At 168 K, a structural phase transition occurs, changing the crystal symmetry point group from cubic (O_h) to orthorhombic (D_{2h})⁵. This phase transition can be assigned to the elastic orientation of the CN^- ions along one of the original $\langle 110 \rangle$ directions of the cubic crystal. The overall cubic symmetry is preserved by the formation of crystalline domains⁶. The elastic alignment of the CN^- ions still allows their reorientation with respect to head and tail (electric dipole moment) by jumps via intermediate $\langle 111 \rangle$ orthorhombic directions⁶. This reorientation process is frozen in at a second phase transition which occurs at 83 K, leaving the crystal in an antiferroelectric state.

The optical and magnetic properties of F centers in KCN have been measured at room temperature^{7,8} but few informations were obtained in the orthorhombic phase below the 168 K where the domains formation causes several experimental problems, especially in the optical absorption measurements. Nevertheless, Ohkura et al.⁹ measured their luminescence spectrum near liquid nitrogen temperature and they suggested that the properties of F centers could be modified in the antiferroelectric phase.

In this letter, we present a more detailed study of the optical properties of F centers between liquid helium temperature and 170 K, and discuss their relation to the antiferroelectric state.

Single crystals of highly zone refined KCN, grown at the crystal growth laboratory of the Physics Department of the University of Utah, were cleaved and mounted in a variable temperature continuous flow cryostat. The samples were irradiated with X rays from a 150 kV,

10 mA tungsten target X ray source, at a temperature near -10°C to avoid M center formation, and with irradiation times from 5 to 40 minutes. The luminescence spectra were analysed with a Jarrell-Ash grating monochromator and

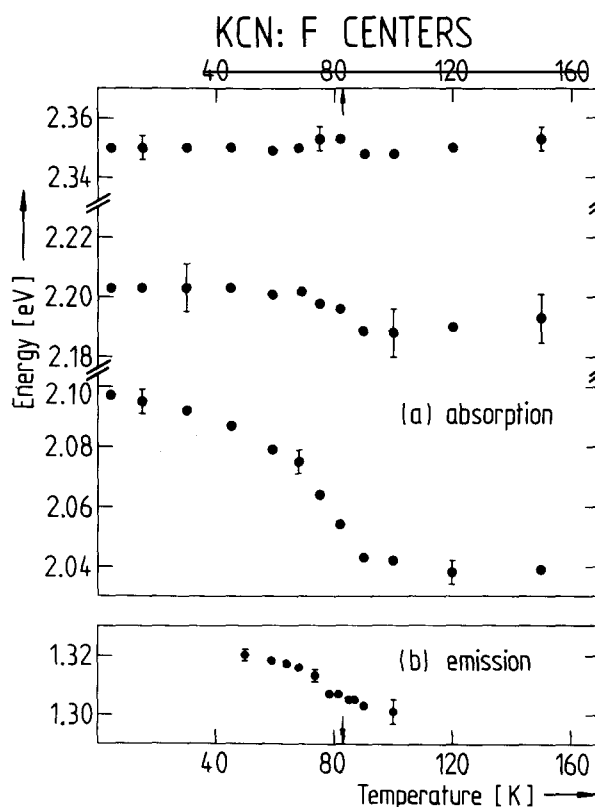


Fig. 1. Absorption and emission spectra of F centers in KCN at 4.5 K. The dots are some measured optical densities. The best fit to all absorption data is shown by the full curve. The three gaussian shaped components of the F absorption band are shown by dashed lines.

*On leave from the Physics Department of the Pontificia Universidade Católica,
Rio de Janeiro, Brazil

detected with a PbS I.R. cell. Excitations were obtained with a 2 mW He-Ne laser.

Because of the strong light scattering of the samples due to the domain structure observed below 168 K, the absorption spectra were measured with a single beam spectrophotometer, in which a short focusing lens was placed just behind the sample. The reference signal was taken in the non irradiated pure crystal at low temperature, allowing direct suppression of the light scattered baseline. Care was taken to avoid distortion of the absorption band due to the I.R. luminescence of the F center by filtering the output light with a KG 3 Schott filter.

Fig. 1 shows the absorption and emission spectra of F centers in KCN at 4.5 K. The emission spectrum has been corrected for optical responses of the instruments. The absorption spectrum was decomposed by computer in three gaussian shaped bands. At 4.5 K, they peak at 2.097 eV, 2.203 eV and 2.350 eV with bandwidth equal respectively to 0.13 eV, 0.15 eV and 0.17 eV. The absorption spectrum changes with temperature but can always be described by three gaussian components. The main effect of temperature is reflected in the spectral location of the three components (fig. 2). The bandwidth of the three components increases slightly with temperature. The luminescence spectrum excited with a 6328 Å He-Ne laser is always a single gaussian shaped band located at 1.325 eV with 0.17 eV bandwidth at 4.5 K. At higher temperatures, there is a shift of the peak position to

longer wavelengths (fig. 2b) but the bandwidth is not affected by the temperature within our experimental errors.

The marked red shift of the lower energy absorption band appears to be strongly connected to particular properties of the antiferroelectric phase ($T < 83$ K). Between 4.5 K and 100 K it is indeed about three times larger than the one measured for the F band in typical alkali halides. Also a marked change occurs near 83 K, at the antiferroelectric phase transition. The smaller red shift of the luminescence band seems to behave in a similar way.

The structure of the absorption band can be understood as follows: When the crystal is cooled down below 168 K, the three $2P$ like Γ_4^- levels of the excited F center, originally degenerated in the cubic symmetry, split in three Γ_2^- , Γ_3^- and Γ_4^- levels in D_{2h} symmetry, giving rise to the three observed bands in the absorption spectrum (fig. 1). According to the symmetry of the deformation of the cubic cell in the structural phase transition at 168 K (tetragonal + trigonal distortion), labelling x, y, z, the three orthorhombic axes so that the corresponding lattice parameters are respectively equal to 6.13, 4.22 and 5.07 Å and if z is the ferroelastic axis, the Γ_4^- level (x axis) has the higher energy and the Γ_3^- level (z axis) the lower one.

Below 83 K, the electric dipole moments of the CN^- ions are all aligned along the ferroelastic axis in an antiferroelectric way. Inversion symmetry at the anion site is lost and

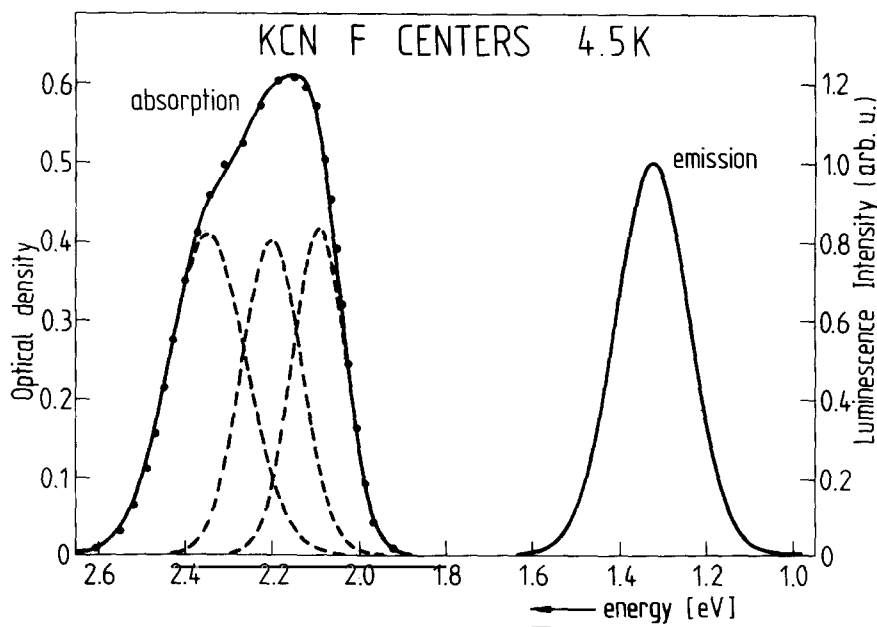


Figure 2 Temperature dependence of the peak position of the three components of the F absorption band (a) and of the emission band (b). The arrow indicates the transition temperature to the antiferroelectric state of the crystal.

theoretical calculations of the lowest energy arrangement gives the symmetry C_{2v} for the anion site⁶. The effect of the temperature on the absorption spectrum can be explained as a temperature dependent internal Stark effect due to the local field. Since the interaction Hamiltonian of the F center electron and the local field transforms like the Γ_1 representation of the C_{2v} group, it will only mix the 2S like (Γ_1) excited state with the $2P_z$ like (Γ_1) excited state leaving unperturbed the Γ_2 and Γ_4 levels¹⁰. Therefore, according to the levels sequence, only the lowest energy absorption band will shift with temperature. The magnitude of the local field can account for this shift, although the 2S and $2P_z$ like states are well separated in energy. In order to explain the sign of the observed energy shift, we conclude that the 2S like excited state lies below the $2P_z$ like state; due to the field mixing they will repel each other and therefore give the right sign of the energy shift of the $2P$ like level¹¹.

The lifetime of the relaxed excited state (R.E.S.) of the F center was measured by recording the decay of the luminescence with a fast storage Tektronix oscilloscope following 1 nsec laser pulse excitation at 2.067 eV. The excitation pulse was obtained from an Electrophotonics model 23 dye laser whose pulse width was sliced to 1 nsec with a Pockel's cell. The decay is exponential on $1\frac{1}{2}$ decades, giving at $T < 10$ K a lifetime of 21.5 ± 2 nsec. This short lifetime is one of the most striking difference between F centers in KCN and in

alkali halides. Calculation of the decay time with the modified Einstein coefficient¹² and assuming the absorption oscillator strength of the order of 1 gives a value of 18 nsec. We conclude that in the RES the 2S and $2P$ like states are probably widely separated so that almost no field mixing exist between them, the emitting state being $2P$ like. On the other hand, the temperature peak shift of the F center luminescence band observed between 4.5 K and 100 K (fig. 2) is of the same order of magnitude as those typically observed in alkali halides; it is therefore hard to decide a priori whether the peak shift of the luminescence in KCN is either due to a thermal process analogous to that known in alkali halides or to a small field mixing with the 2S like state of even both phenomena. Furthermore, we are not yet able to decide whether the symmetry of the emitting state would allow field mixing with the 2S like Γ_1 state.

Finally, the excitation spectra of the F luminescence was measured and the result showed also the three gaussian shaped components. Their relative intensities are different from those observed in absorption, the lower energy band being strongly favoured with respect to the other two.

Acknowledgments - We are grateful to Prof. Fritz Lüty for kindly supplying the samples for these experiments and the Swiss National Science Foundation for financial support. One of us (JFW) is grateful to the Department of Physics of the Pontificia Universidade Católica, for financial aid.

REFERENCES

1. PARRY G.S., *Acta Crystallographica* **15**, 596 (1962).
2. SUGA H., MATSUO T. and SEKI S., *Bulletin of the Chemical Society of Japan* **38**, 1115 (1965).
3. GONGORA A., JULIAN M. and LÜTY F., *Proceedings of the International Conference on Low Lying Lattice Vibrational Modes and their Relationship to Superconductivity and Ferroelectricity*, Puerto Rico (1975).
4. DULTZ W., *Journal of Chemical Physics* **65**, 7, 2812 (1976).
5. Group theory notations from : KOSTER G.F., DIMMOCK J.O., WHEELER R.G. and STATZ H., *Properties of the Thirty-Two Point Groups*, M.I.T. Press, Cambridge Mass. (1963).
6. von der WEID J.-P., SCAVARDA DO CARMO L.C., COSTA RIBEIRO S., dos SANTOS R.R., KOILLER B. and CHAVES A.S., *Journal de Physique* **37**, 12, C7-241 (1977).
7. SCAVARDA DO CARMO L.C. and COSTA RIBEIRO S., *Journal of Physics C* **8**, L527 (1975).
8. PANEPUCCI H., ROBERT R., FARACH H.A. and de SOUZA M., *Solid State Communications* **16**, 1147 (1975).
9. OHKURA H., SCAVARDA DO CARMO L.C., KALINOWSKI H.J. and COSTA RIBEIRO S., *Journal of the Physical Society of Japan* **41**, 5, 1805 (1976).
10. The other possible antiferroelectric structures give C_2 symmetry for the anion site. The $2P_x$ and $2P_y$ like states transform like the Γ_2 irreducible representation so that they are always unperturbed by the local field.
11. Recent absorption measurements seem to confirm this point of view. Due to field mixing, the $1S \rightarrow 2S$ forbidden transition becomes partially allowed when the temperature is lowered. We observed indeed a band growing at 825 nm for $T < 83$ K which would indicate that the splitting between the 2S and $2P_z$ like levels is about 0.5 eV above 83 K.
12. FOWLER W.B. and DEXTER D.L., *Physical Review* **128**, 5, 2154 (1962).